The Corrosion and Electrical Properties of Steels.

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As long ago as 1899, Caspari* showed that the condition that zinc should dissolve in an acid solution with evolution of hydrogen may be expressed in the form—

Single potential of metal + overvoltage < single potential of hydrogen electrode. (*a*)

The single potential of zinc in a normal zinc sulphate solution is $-0{\cdot}493$ volt, and that of a hydrogen electrode in normal sulphuric acid is $+0{\cdot}277$ volt. If a mixture of zinc sulphate and sulphuric acid be taken, the potential of the zinc will become more positive as the concentration of zinc sulphate increases, and the potential of the hydrogen electrode more negative as the concentration of the acid decreases. Since the overvoltage of pure zinc is about 0·7 volt, conditions may be easily adjusted in this way so that solution is exactly arrested and the statement (*a*) above then becomes an equation.

If a definite solution is used for a series of experiments, then the potential of the hydrogen electrode is constant, and the tendency of the metal to dissolve will be measured by the fixed potential of this hydrogen electrode minus the sum of the overvoltage and the potential of the metal.

Denoting this "solution voltage" by the letter S, we may say generally that the condition that any metal shall dissolve with evolution of hydrogen in the given solution is

$$S > 0,$$

and, further, that the rate of solution of the metal is approximately proportional to the value of S.

In order to apply this method of reasoning to the problem of steel corrosion, two assumptions have to be made:—

(1) That the corrosion factor of a given steel is proportional to its rate of solution in a given acid.

(2) That the rate of corrosion without evolution of gas is controlled by similar laws to that with evolution of gas.

If these assumptions are even approximately true, then it should be

* 'Zeit. Physik. Chem.,' vol. 30, p. 89 (1899).

possible to obtain a good estimate of the corrosion factor of a given steel by a simple measurement of its overvoltage and single potential in a given acid.

The work described in this communication was undertaken with the idea of examining how far, if at all, these assumptions were justifiable.

Varieties of Steel Used.

The samples of steel taken were 15 in number, all forged bars, 1 inch diameter and 5 inches long. Discs of $\frac{1}{4}$-inch thickness were sawn off each bar, and a small segment of about 1 cm. chord sawn off each disc. The samples were numbered as follows:—

Steel No.	Type of steel.
S.C.I.	Pure iron.
2229	Carbon steel, low.
2228	Carbon steel, medium.
1618/2	Carbon steel, medium.
898 M/13	Silicon iron alloy.
3433/2	High chromium alloy.
1775	Nickel chromium steel, low carbon.
1795 C	Nickel chromium steel, medium carbon.
1663 S	Nickel chromium steel, high carbon.
3137 D	Nickel chromium steel, high carbon.
3125	Nickel steel, 5 per cent. Ni.
3408	Nickel steel, 36 per cent. Ni.
1908 D	Tungsten steel.
3435	Tungsten cobalt steel.
1109 D	"Resista," an alloy of 5 per cent. Mn and 15 per cent. Ni.

Full analyses, showing the compositions of these various steels, are given in the Table on p. 58.

Overvoltage Measurements.

The small segments of steel were smoothed on an emery wheel and a uniformity of surface secured by rubbing on No. 1 emery cloth. This uniformity of surface is necessary for comparative purposes, as the overvoltage is affected to a small extent by the nature of the surface.*

A short copper wire was soldered to each and covered with white, hard sealing wax, leaving only 1 sq. cm. of the steel uncovered. The overvoltage was then measured by the Back E.M.F. method, as described in 'Trans. Chem. Soc.,' vol. 105, p. 2420 (1914), the electrolyte being N/1 H_2SO_4.

Four series of measurements were made with current densities from 2 to 2000 milliampères per square centimetre, and the averages of these four sets

* Pring and Curzon, 'Faraday Soc. Trans.,' 1911.

Summary of Analyses of Specimens.

Type of steel.	Steel No.	Treatment. ° C.	Analysis.								
			C.	Si.	S.	P.	Mn.	Cr.	Ni.	W.	Co.
Pure iron	S.C.I.	As forged	·03	·01	·013	·014	·04				
Carbon steel	2229	,,	·29	·31	—	—	·48				
Carbon steel	2228	,,	·50	·05	—	—	·04				
Carbon steel	1618/2	,,	·54	·16	—	—	1 ·03				
Silicon material	898 M/13	,,	·11	3 ·05	·043	·022					
Chromium steel (high Chromium)	3433/2	775° Furnace	·29	—	—	—	—	12 ·84			
Nickel steel	3125	As forged	·28	—	—	—	·50	—	5 ·00		
Nickel steel	1798 H	830° Furnace	·48	—	—	—	1 ·35	—	19 ·58		
Nickel steel	34[illegible]8	As forged	·05	·05	·27	·08	·28	—	36 ·38		
Nickel chromium steel	1775	,,	·12	—	—	—	·13	1 ·81	3 ·41		
Nickel chromium steel	1795 C	795° Furnace	·34	·10	·045	·041	·42	1 ·79	3 ·43		
Nickel chromium steel	1663 S	795° Furnace	·65	·12	—	—	·12	2 ·00	2 ·00		
Nickel chromium steel	3137 D	795° Furnace	·66	·12	—	—	·12	2 ·50	2 ·75		
"Resista" (Fe-Ni-Mn alloy)	1109 D	As forged	·60	—	—	—	5 ·00	—	15 ·00		
Tungsten chromium steel	1908 D	795° Furnace	·60	—	—	—	·20	4 ·00	—	17 ·0	
Tungsten chromium cobalt steel	3435	775° Furnace	·31	—	—	—	—	3 ·62	—	16 ·1	4 ·90

of readings are given in the following Table, the current density being given in milliampères per square centimetre and the overvoltage in volts.

Current density.	S.C.I.	2229	2228	1618/2.	898 M/13.	3433/2.	1775.	1795 C.
2	0·24	0·23	0·20	0·21	0·22	0·26	0·20	0·18
4	0·25	0·23	0·21	0·21	0·22	0·26	0·20	0·19
6	0·26	0·23	0·22	0·21	0·22	0·26	0·21	0·19
10	0·26	0·24	0·22	0·22	0·22	0·26	0·21	0·19
20	0·27	0·24	0·22	0·22	0·22	0·26	0·21	0·19
50	0·27	0·24	0·23	0·22	0·22	0·27	0·22	0·20
100	0·27	0·24	0·23	0·22	0·22	0·27	0·22	0·19
200	0·27	0·24	0·22	0·22	0·22	0·27	0·22	0·19
400	0·28	0·24	0·22	0·21	0·22	0·27	0·22	0·18
1000	0·27	0·24	0·21	0·20	0·21	0·28	0·21	0·17
2000	0·26	0·23	0·21	0·19	0·20	0·27	0·20	0·16

Current density.	1663 S.	3137 D.	3125.	3408.	1908 D.	3435.	1109 D.
2	0·19	0·19	0·18	0·20	0·21	0·21	0·19
4	0·19	0·20	0·19	0·22	0·22	0·22	0·20
6	0·20	0·21	0·19	0·22	0·22	0·23	0·20
10	0·20	0·21	0·20	0·23	0·23	0·24	0·21
20	0·20	0·22	0·20	0·23	0·23	0·24	0·21
50	0·21	0·22	0·21	0·23	0·23	0·25	0·21
100	0·21	0·23	0·21	0·22	0·24	0·25	0·21
200	0·21	0·23	0·21	0·21	0·24	0·25	0·21
400	0·21	0·23	0·21	0·20	0·24	0·25	0·20
1000	0·21	0·23	0·19	0·18	0·23	0·25	0·19
2000	0·20	0·22	0·18	0·17	0·22	0·23	0·18

Single Potential Measurements.

After measuring the overvoltage, the electrodes were washed with distilled water, dried, and repolished with emery cloth as before. The potential of each was then measured in a N/1 H_2SO_4 electrolyte against a mercurous sulphate electrode containing the same solution. Measurements were made by means of the same apparatus as used for overvoltage, the anode A being disconnected, and readings taken every minute for 5 to 10 minutes until constant for 3 consecutive minutes. Measurements were also taken in an electrolyte consisting of N/1 $FeSO_4$ + N/1 H_2SO_4, but no appreciable difference was observed. After deducting the difference of potential between a normal mercurous sulphate electrode and a normal hydrogen electrode, the following values were obtained for the single potentials of the steels against a standard hydrogen electrode :—

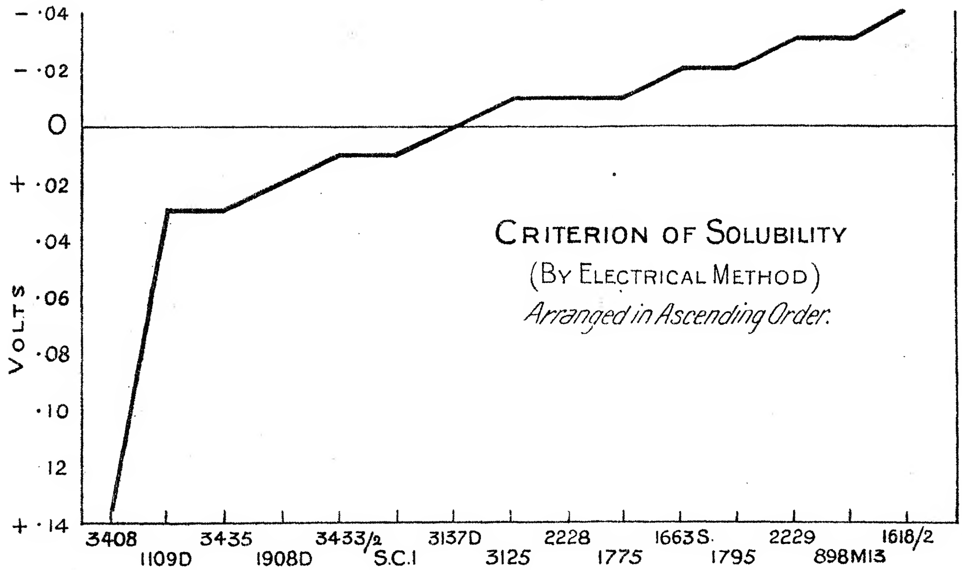
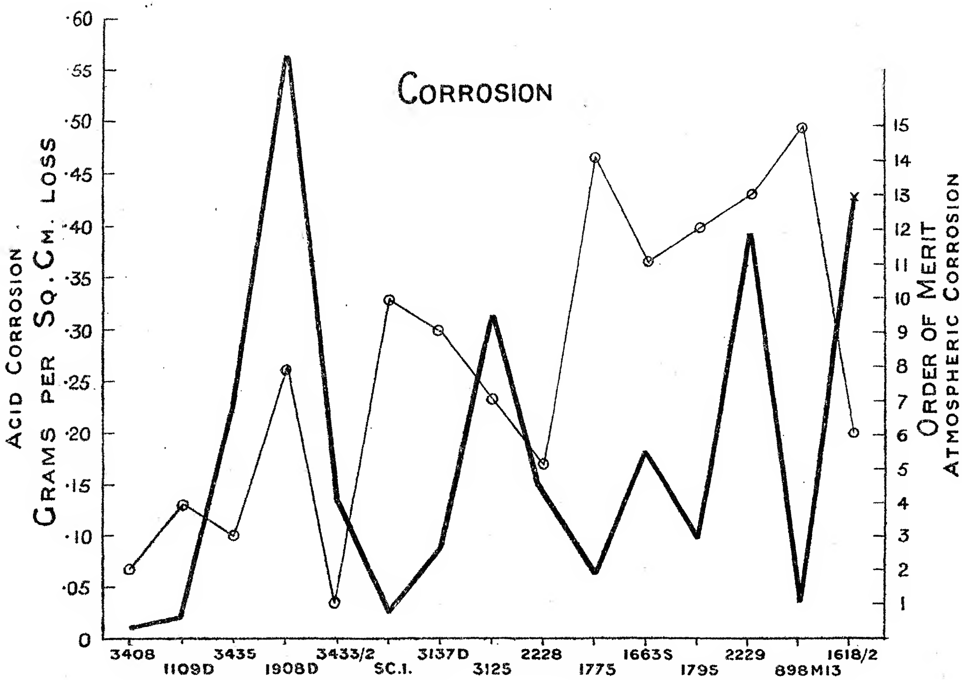


FIG. 1.



—— Normal H_2SO_4, 72 hours. —— Atmospheric, 10 weeks.

FIG. 2.

Steel.	Potential.	Steel.	Potential.	Steel.	Potential.
	volt.		volt.		volt.
S.C.I.	−0·23	3433/2	−0·25	3125	−0·19
2229	−0·26	1775	−0·21	3408	−0·06
2228	−0·21	1795 C	−0·20	1908 D	−0·19
1618/2	−0·25	1663 S	−0·21	3435	−0·18
898 M/13	−0·25	3137 D	−0·19	1109 D	−0·16

In order to combine these measurements with the overvoltage measurements, the question arises as to what current density should be taken as standard. Since the local currents set up during most forms of steel corrosion are probably very feeble, it is perhaps advisable to take the values for the overvoltage at the lowest current densities used. On adding these overvoltages to the corresponding single potentials, we obtain the values of −S* for each electrode. These are arranged in order of magnitude in the following Table :—

No.	Steel.	−S.	No.	Steel.	−S.
		volt.			volt.
1	3408	+0·14	9	2228	−0·01
2	1109 D	+0·03	10	1775	−0·01
3	3435	+0·03	11	1663 S	−0·02
4	1908 D	+0·02	12	1795 C	−0·02
5	3433/2	+0·01	13	2229	−0·03
6	S.C.I.	+0·01	14	898 M/13	−0·03
7	3137 D	0·00	15	1618/2	−0·04
8	3125	−0·01			

Corrosion in Acid.

For these measurements, the larger segments of the discs cut off from the bars were used. One face of each disc was smoothed down on a carborundum wheel, rubbed with emery as before, weighed carefully, and the remainder of the disc covered with a coating of wax. All the discs were then laid, polished side up, on the bottom of a large glass dish, and 3 litres of $N/1$ H_2SO_4 poured in, the temperature being $15 \pm 1°$ C. throughout the whole experiment.

After 72 hours the discs were removed, washed, the wax cleaned off, and the discs dried and weighed. The loss in weight per square centimetre of exposed surface is given in the following Table :—

* While S measures the corrodibility, −S measures the resistance to corrosion. The Table is arranged in this way in order to correspond with the other Tables.

Departure of Order of Merit Figures from those for Atmospheric Corrosion.

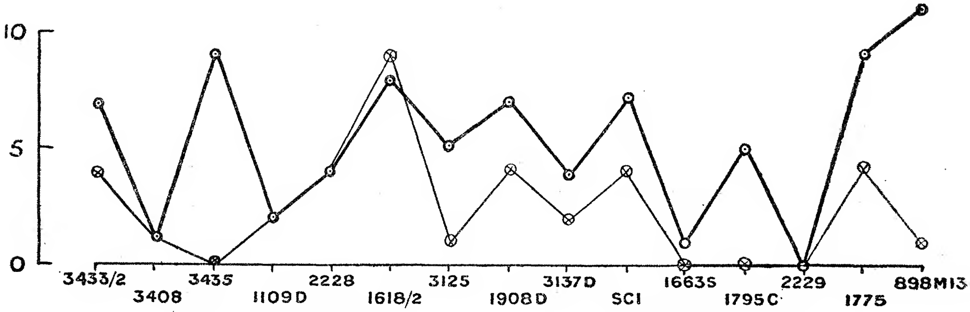


Fig. 3.

Order of Merit—Resistance to Corrosion.

(The Specimens are arranged in order of Resistance to Atmospheric Corrosion.)

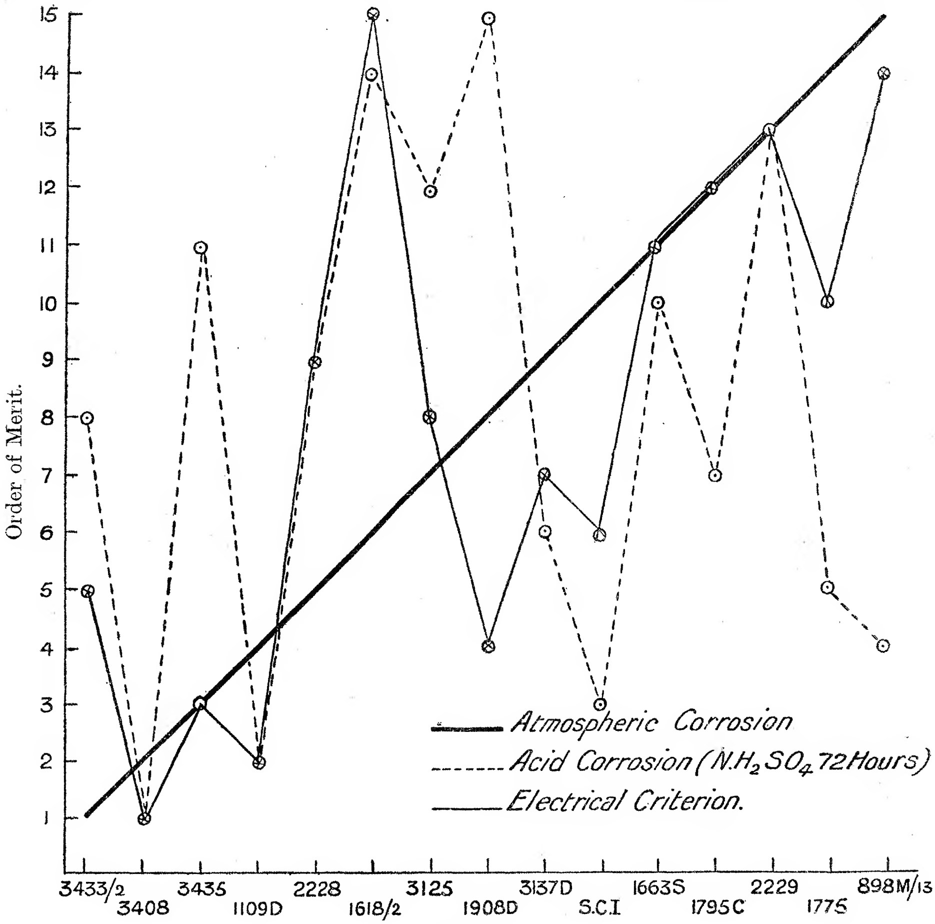


Fig. 4.

Steel.	Loss in grm.	Steel.	Loss in grm.	Steel.	Loss in grm.
S.C.I.	0·024	3433/2	0·132	3125	0·314
2229	0·400	1775	0·062	3408	0·008
2228	0·142	1795 C	0·096	1908	0·564
1618/2	0·432	1663 S	0·182	3435	0·230
898 M/13	0·034	3137 D	0·088		

Atmospheric Corrosion.

The steel bars from which the discs had been sawn off were placed in a horizontal row in a box with the worked ends protruding and left exposed to the laboratory atmosphere for 10 weeks during the months of May, June, and July. At the end of that time none of the bars showed any appreciable rust except on the worked ends, and since patches on these ends had been polished by the rubbing action of the upper part of the saw, the variation in corrodibility of the polished and rough metal could be observed. They were carefully examined with the aid of a Coddington lens and arranged in order of corrodibility, as follows:—

No.	1	3433/2	Quite bright. No rust.
„	2	3408	Faint, but uniform light brown coloration.
„	3	3435	Bright, slight traces of rust.
„	4	1109 D	Bright, rusting a little more marked.
„	5	2228	Bright, patches of rust visible.
„	6	1618/2	Polished parts bright, large rust patches.
„	7	3125	Polished parts bright, larger rust patches.
„	8	1908 D	Polished parts bright, rest covered with rust.
„	9	3137 D	Polished parts black, rest covered with rust.
„	10	S.C.I.	Polished parts black and partly rusted, rest quite rusted.
„	11	1663 S	Polished parts black and much rusted.
„	12	1795 C	Quite covered with rust, thin over polished parts.
„	13	2229	Quite covered with rust, polished parts not visible.
„	14	1775	Badly rusted, thick uniform coating.
„	15	898 M/13	Badly rusted, thick uniform coating.

The Table on p. 64 shows the order of resistance to corrosion of the steels as determined by these three methods.

If the object of experiments on corrosion be considered to be the determination of the alloys which best resist the action of the atmosphere, then the figures in the third column of the Table must be taken as standard, and those in the other columns judged as good or bad according to their nearness or otherwise to those in the third.

Reviewing the Table as a whole, in four cases the electrical and acid methods give identical results, in 10 cases the electrical method gives better results than the acid method, and in one case only (No. 1618/2), the acid

Steel No.	Electrical method.	Corrosion in acid.	Atmospheric corrosion.
S.C.I.	6	3	10
2229	13	13	13
2228	9	9	5
1618/2	15	14	6
898 M/13	14	4	15
3433/2	5	8	1
1775	10	5	14
1795 C	12	7	12
1663 S	11	10	11
3137 D	7	6	9
3125	8	12	7
3408	1	1	2
1908 D	4	15	8
3435	3	11	3
1109 D	2	2	4

method gives a slightly better estimate than the electrical though both are wide of the mark. This is evidently due to the presence of 1 per cent. Mn in the specimen, since this metal is only attacked slowly by the atmosphere owing to the formation of a protective oxide coating, while it dissolves with ease in acid and also has a high negative solution potential.

In four cases only does the electrical method agree with atmospheric corrosion, but the acid method only agrees in one case and the deviations are generally much greater with this method.

Notes on Individual Alloys.

S.C.I., Pure Iron.—The resistance of this to the action of acid seems to be connected with its high overvoltage, and its non-resistance to atmospheric corrosion may be due to the presence of some substance in the air which reduces the overvoltage. After treatment with acid the surface was quite smooth but dull.

2229, *Low Carbon Steel.*—In this case only, all three methods agree in showing the alloy to be very liable to corrosion. Large patches were eaten out by the acid.

2228, *Medium Carbon Steel.*—Both electrical and acid methods under-estimate the corrosion-resisting powers of this alloy. The surface was pitted by the acid in patches.

1618/2, *Medium Carbon Steel,* 1 *per cent. Mn.*—This has already been referred to. The surface was very deeply pitted and eaten into by the acid.

898 M/13, *Silicon Iron Alloy.*—The acid test in this case gives a very false impression as to the corrodibility. The surface remained smooth and bright. The electrical method gives a much better idea.

3433/2, *High Chromium Alloy.*—Here again, both methods greatly underestimate the corrosion-resisting powers of this alloy, the acid method giving the more incorrect estimate, the surface being decidedly pitted after treatment. This was the only alloy which was quite unchanged by the atmospheric test.

1775, *Cr Ni Steel, Low Carbon.*—The corrodibility is underestimated by the electrical method and very badly by the acid method. After treatment with acid the surface was almost smooth. With this exception, all the nickel steels have been well placed by the electrical method, while half of them are badly placed by the acid method.

1795 C was slightly pitted, 1663 S deeply pitted, and 3137 D left almost smooth by the acid test.

3125, *Nickel Steel,* 5 *per cent. Ni,* was very badly attacked by the acid, specially round the edges. Though the overvoltage is low, the negative single potential is also low, and hence the electrical method places this alloy much higher on the scale than the acid method, and nearer the value indicated by atmospheric corrosion.

3408, *Nickel Steel,* 36 *per cent. Ni.*—The low negative single potential of this alloy, due to the high percentage of nickel, places it easily first by the electrical method, and its appearance was quite unchanged by the acid test. In the atmosphere the coloration produced is probably due to a thin protective coating of nickel oxide.

1908 D, *Tungsten Steel.*—The ready solubility of this, and also of No. 3435, which also contains tungsten, is surprising. Both have fairly high overvoltages and low negative single potentials, and hence the electrical method gives a much better estimate of the corrosion-resisting powers.

1109 D, *Manganese Nickel Steel.*—The figure for the acid test with this alloy is doubtful, as owing to the extreme toughness a disc could not be cut off, and the experiment was made with a small chipping.

Advantages and Disadvantages of the Electrical Method.

(a) *Advantages:*—

1. This method certainly gives a better estimate of the ability of an alloy to resist atmospheric corrosion than the acid immersion method.

2. When once the apparatus is fitted up a sample can be examined in 10–30 minutes, while at least two hours is necessary for the acid test.

3. By the addition of certain elements with the object of raising the overvoltage and of others with the object of lowering the negative single potential, there appears to be a better chance of attaining the ideal of a rustless steel than by merely trusting to a single measurement for determining corrodibility.

4. Very small samples, less than 1 grm., may be used.

(b) *Disadvantages*:—

1. The apparatus needed is much more complicated and expensive than that required for the acid test, and greater skill in manipulation is necessary.

2. The differences in the values of S obtained are not great enough for suitable grading of the alloys.

3. Slight errors in measurement may cause large differences of position in the corrodibility scale.

4. Where a large number of samples have to be tested at the same time, the acid immersion method can probably be worked more quickly, specially as the electrodes for the electrical method require careful preparation.

The overvoltage apparatus (*loc. cit.*) can be considerably simplified. The voltmeter V may be dispensed with, and the potentiometer P_2 replaced by a sliding resistance coil. A calomel or mercurous sulphate electrode may be used instead of the more troublesome hydrogen electrode, a unipivot galvanometer may replace the reflecting galvanometer and shunt G, and the commutator **X** can be fixed directly on the spindle of a small electromotor and driven easily at a high speed.

It may be better to use still lower current densities, say from 0·1 to 10 milliampères per square centimetre and extrapolate to find the overvoltage at zero current density. Possibly also the measurement of the overvoltage and the single potential in a solution of a weaker acid such as acetic may give results more comparable with atmospheric corrosion and also give greater variation in the values of S obtained. The liability to atmospheric corrosion is reduced by polishing the surface of a metal, owing to the fact that the overvoltage is raised, and it is generally true that any process or addition which raises the overvoltage of a metal also reduces its tendency to corrode. The galvanising of iron is a case in point, zinc having a very high overvoltage.

There are, of course, so many different causes of corrosion that one cannot hope for a method which will give reliable information on corrodibility in all cases. Again, referring to the comparison Table, we see that the electrical method only places one alloy more than four out, while the acid method makes nine such mistakes out of the 15 cases. At the same time, in five cases the electrical method makes a mistake of four places, and this cannot be regarded as satisfactory. It is hoped that the method may be further developed so as to give more reliable information.

Other points which might be considered are:—

(1) The average overvoltage.

(2) The maximum overvoltage.

(3) The current density required to produce maximum overvoltage, but

conclusions deduced from such considerations would not have the same theoretical foundation as those obtained by the method already described.

It is evident that the assumptions made at the beginning of this paper are only fulfilled to a small extent. The first is certainly somewhat wide of the facts if the given acid is N/1 H_2SO_4. It may be nearer the mark when some other acids are used, and it is possible that, with suitable choice of solvents, reliable information may be obtained with regard to corrodibility under different circumstances. The present paper deals only with atmospheric corrosion, and the conclusions arrived at are not intended to apply to other cases (sea water, strong acids, etc.). The second of the two assumptions appears more justifiable than the first, as it is largely on this second that the electrical method is based. The solution or corrosion of a metal is intimately associated with the exchange of electrical charges, and the tendency to corrosion is measured by the potential differences between these charges. When the acid test is employed, the overvoltage of the sample is considerably lowered as soon as the surface becomes attacked, and local currents are set up due to slight non-homogeneity of the alloy, thus greatly increasing the rate of solution. In the electrical method, the surface of the metal or alloy is quite unchanged during the overvoltage measurements if the current density is kept low, and is not appreciably affected by the five minutes' acid immersion when the single potential is measured. Hence the resistance of the alloy to the beginning of corrosion is determined, and it must, of course, be remembered that this is not usually the same after corrosion has once started.

There is no reason why the electrical method should not be employed with non-ferrous alloys and metals, but further experiment with different electrolytes is needed before any standardisation will be possible.

A recent paper by one of the writers of the present paper is given in the 'Journal of the Iron and Steel Institute,' No. 1, 1916, entitled "The Influence of Carbon and Manganese upon the Corrosion of Iron and Steel." Much useful information with regard to the effect of tap water and sea water is there presented.